254. *The Microwave Spectrum, Structure, and Nuclear Quadrupole Coupling Coefficients of Nitrosyl Chloride.*

By D. J. Millen and J. Pannell.

Nitrosyl chloride enriched in ^{18}O has been prepared and, from its microwave spectrum, rotational constants have been evaluated. These have been combined with those of the ^{35}Cl and ^{37}Cl isotopic species of normal nitrosyl chloride to yield the molecular dimensions: $r_{N-Cl} = 1{\cdot}975$ Å, $r_{N-O} = 1{\cdot}139$ Å, and $\angle ONCl = 113° 20'$. From the hyperfine structure of the spectra, chlorine nuclear quadrupole coupling parameters, $eQ.\partial^2V/\partial a^2 = -48{\cdot}7$, $eQ.\partial^2V/\partial b^2 = 29{\cdot}4$, and $eQ.\partial^2V/\partial c^2 = 19{\cdot}3$ Mc./sec. were obtained for $N^{16}O^{35}Cl$, and $eQ.\partial^2V/\partial a^2 = -38{\cdot}4$, $eQ.\partial^2V/\partial b^2 = 23{\cdot}2$, and $eQ.\partial^2V/\partial c^2 = 15{\cdot}2$ Mc./sec. for $N^{16}O^{37}Cl$. The coupling parameters have been interpreted in terms of bond properties, and comparison made with nitryl chloride. It is concluded that the nitrogen–chlorine bond is not only appreciably more ionic (in the sense NO^+Cl^-) but also has more double-bond character than the corresponding bond in nitryl chloride.

An apparatus is described for the preparation of ^{18}O-enriched oxygen by electrolysis of about 0·6 ml. quantities of water, leaving a residue of only 0·1 ml.

The rotational constants of two isotopic species of a triatomic molecule provide in principle sufficient information to determine the molecular dimensions completely. In the case of nitrosyl chloride, however, the two species $NO^{35}Cl$ and $NO^{37}Cl$ which are readily examined in natural abundance do not permit a unique structure to be pin-pointed with useful precision; pairs of N–Cl and N–O distances over an appreciable range are compatible with the observed rotational constants. A similar situation has been reported for nitrosyl bromide.[1]

To overcome this difficulty the species $N^{18}OCl$ has been prepared, and its microwave spectrum analysed. By combining the rotational constants thus obtained with those derived from the microwave spectra of $N^{16}O^{35}Cl$ and $N^{16}O^{37}Cl$ the structural parameters have been determined. The orientation of the principal axes of inertia with respect to the

Table 1. *Spectrum of* $N^{16}O^{35}Cl$. *Assignments, relative intensities, and comparisons of observed and calculated frequencies.* (*F_f and F_i are the final and initial total angular momentum quantum numbers.*)

						Frequency (Mc./sec.)		Relative
J'		J	F_f		F_i	obs.	calc.	intensity
1_{01}	←	0_{00}	3/2	←	3/2	11,104·15	11,104·15	52·5
			5/2	←	3/2	11,116·33	11,116·33	100·0
			1/2	←	3/2	11,126·05	11,126·06	20·8
2_{12}	←	1_{11}	5/2	←	3/2	21,857·42	21,857·32	52·5
			3/2	←	3/2	21,860·70	21,860·67	26·7
			5/2	←	5/2	21,864·59	21,864·57	22·5
			7/2	←	5/2	21,869·39	21,869·40	100
			3/2	←	1/2	21,873·93	21,873·90	20·8
			1/2	←	1/2	21,879·07	21,878·73	20·8
2_{02}	←	1_{01}	5/2	←	5/2	22,215·08	22,215·42	22·5
			3/2	←	1/2		22,214·38	20·8
			5/2	←	3/2	22,227·37	22,227·59	52·5
			7/2	←	5/2		22,227·39	100
			3/2	←	3/2	22,236·45	22,236·29	26·7
2_{11}	←	1_{10}	5/2	←	3/2	22,580·47	22,579·78	52·5
			3/2	←	3/2	22,585·47	22,585·03	26·7
			5/2	←	5/2		22,584·60	22·5
			7/2	←	5/2	22,592·95	22,591·95	100
			3/2	←	1/2		22,593·71	20·8
			1/2	←	1/2	22,601·72	22,601·06	20·8

---

[1] Weatherly and Williams, *J. Chem. Phys.*, 1956, **25**, 717.

TABLE 2. *Spectrum of* $N^{16}O^{37}Cl$. *Assignments, relative intensities, and comparison of observed and calculated frequencies.*

						Frequency (Mc./sec.)		Relative intensities
J'		J	F_f		F_i	obs.	calc.	
1_{01}	←	0_{00}	3/2	←	3/2	10,849·36	10,849·37	52·5
			5/2	←	3/2	10,858·96	10,858·97	100·0
			1/2	←	3/2	10,866·65	10,866·65	20·8
2_{12}	←	1_{11}	5/2	←	3/2	21,362·64	21,362·06	52·5
			3/2	←	3/2	21,364·7	21,364·67	26·7
			5/2	←	5/2	21,367·47	21,367·96	22·5
			7/2	←	5/2	21,371·53	21,371·66	100
2_{11}	←	1_{10}	5/2	←	3/2	22,052·07	22,051·67	52·5
			3/2	←	3/2	22,056·03	22,055·88	26·7
			5/2	←	5/2		22,055·37	22·5
			7/2	←	5/2	22,062·26	22,061·27	100
			3/2	←	1/2		22,062·54	20·8
			1/2	←	1/2	22,068·11	22,068·44	20·8
2_{02}	←	1_{01}	5/2	←	5/2	21,703·77	21,703·77	22·5
			3/2	←	1/2		21,702·95	20·8
			5/2	←	3/2	21,713·25	21,713·33	52·5
			7/2	←	5/2		21,713·33	100
			3/2	←	3/2	21,719·68	21,720·23	26·7

TABLE 3. *Spectrum of* $N^{18}O^{35}Cl$. *Assignments, relative intensities, and comparison of observed and calculated frequencies.*

						Frequency (Mc./sec.)		Relative intensity
J'		J	F_f		F_i	obs.	calc.	
1_{01}	←	0_{00}	3/2	←	3/2	10,532·72	10,532·72	52·5
			5/2	←	3/2	10,544·88	10,544·92	100
			1/2	←	3/2	—	10,554·68	20·8
3_{13}	←	2_{12}	9/2	←	7/2	31,123·80	31,123·75	100
			5/2	←	5/2		31,124·96	14·6
			3/2	←	1/2		31,123·67	28
			7/2	←	5/2	31,121·14	31,120·72	68·6
			5/2	←	3/2		31,120·63	44·8
3_{03}	←	2_{02}	9/2	←	7/2	31,623·50	31,623·50	100
			7/2	←	5/2		31,623·50	68·6
			3/2	←	5/2	31,620·48	31,620·49	0·8
			3/2	←	1/2		31,620·49	28
			7/2	←	7/2	31,611·34	31,611·37	11·4
			5/2	←	5/2	31,628·97	31,629·17	14·6
			3/2	←	3/2	31,632·28	31,632·62	11·2
3_{12}	←	2_{11}	9/2	←	7/2	32,132·36	32,132·28	100
			7/2	←	5/2	32,129·17	32,129·25	68·6
			5/2	←	3/2		32,129·25	44·8
2_{20}	←	3_{21}	5/2	←	3/2	31,632·28	31,632·28	44·8
			3/2	←	3/2		31,632·28	11·2
			7/2	←	5/2		31,623·58	68·6
			5/2	←	5/2	31,623·50	31,623·58	14·6
			3/2	←	5/2		31,623·58	0·8

molecular geometry has been settled at the same time. The nuclear quadrupole coupling coefficients which have been evaluated from the hyperfine structure refer to these axes, and the directional relationship had to be established before the nuclear quadrupole coupling could be related to bond properties.

The Spectrum.—The nitrosyl chloride molecule approximates closely to a near prolate symmetric rotor, the $\Delta J = 1$, $\Delta K = 0$ transitions falling in the regions of approximately 10, 20, and 30 kMc./sec. for J,1 ← 0, 2 ← 1, and 3 ← 2 transitions respectively. Because these lines are comparatively weak, a highly enriched (~90%) sample of the O^{18} species was prepared. The spectra of $N^{16}O^{35}Cl$ and $N^{16}O^{37}Cl$ were observed by using a normal sample. The spectra showed quadrupole hyperfine structure arising from the chlorine nucleus, but that due to the nitrogen nucleus was not resolved. The frequencies and assignments for the three isotopic species $N^{16}O^{35}Cl$, $N^{16}O^{37}Cl$, and $N^{18}O^{35}Cl$ are recorded in the Tables.

The values for the $J,2 \longrightarrow 1$ transitions of $N^{16}O^{35}Cl$ and $N^{16}O^{37}Cl$ are in good agreement with those previously reported.[2] The observation of the $J,1 \longleftarrow 0$ transitions provides $B + C$ directly and leads to improved values for the nuclear quadrupole coupling coefficients.

The hyperfine structure may be described in terms of the coupling coefficients eQq_{aa}, eQq_{bb}, and eQq_{cc}, where e is the proton charge, Q the quadrupole moment of the chlorine nucleus, and q_{aa}, q_{bb}, and q_{cc} the molecular electric field gradients at the chlorine nucleus along the *a*-, *b*-, and *c*-axes of inertia. The hyperfine patterns were analysed according to first-order perturbation treatment for a near symmetric rotor.[3] It was found sufficient to retain only linear terms in the asymmetry parameter b. The coefficient eQq_{aa}, which refers to that principal axis, which is a near rotational symmetry axis, was obtainable directly from the $J,1 \longleftarrow 0$ transitions. The components of the higher J transitions were also used to obtain best values. Rotational transitions involving $K = 1$ levels have hyperfine structures which are determined in part by the remaining independent coefficient to be evaluated. For $N^{18}O^{35}Cl$ in which the transition $J,3 \longleftarrow 2$ was studied, eQq_{aa} was found to be −48·8 Mc./sec., but the splitting was too small to allow the other coefficients to be evaluated. The coefficients are given in Table 4.

TABLE 4. *Nuclear quadrupole coupling parameters.*

	eQq_{aa} (Mc./sec.)	eQq_{bb} (Mc./sec.)	eQq_{cc} (Mc./sec.)	η
$N^{16}O^{35}Cl$	−48·7	29·4	19·3	−0·207
$N^{16}O^{37}Cl$	−38·4	23·2	15·2	−0·207

The rotational constants were then calculated from the frequencies corrected for nuclear quadrupole perturbation. Values for $B + C$ were obtained directly from the $J,1 \longleftarrow 0$ transitions and confirmed by the $K = 0$ components of the $J,1 \longleftarrow 2$ transitions. The separation of the $K = 1$ components of $J,2 \longleftarrow 1$ or $3 \longleftarrow 2$ transitions yielded values for $B - C$. The rotational parameters are listed for the three molecular species in Table 5.

TABLE 5. *Rotational parameters.*

	C (Mc./sec.)	B (Mc./sec.)	A (Mc./sec.)	b
$N^{16}O^{35}Cl$	5376·39	5737·50	85,420	$-2{\cdot}261 \times 10^{-3}$
$N^{16}O^{37}Cl$	5256·17	5600·88	85,400	$-2{\cdot}155 \times 10^{-3}$
$N^{18}O^{35}Cl$	5103·17	5439·31	82,580	$-2{\cdot}174 \times 10^{-3}$

No transition was observed from which the large rotational constant could be evaluated directly; the value reported is that calculated on the basis of a rigid planar molecule. The asymmetry parameter b has been calculated on the same assumption. The moments of inertia calculated from these values are given in Table 6. Tables 1, 2, and 3 show that the frequencies calculated in terms of these rotational parameters and the nuclear quadrupole coupling coefficients in Table 4 are in close agreement with the observed frequencies.

TABLE 6. *Moments of inertia* (a.m.u. Å^2).

	I_c	I_b	I_a
$N^{16}O^{35}Cl$	94·0283	88·1103	5·9180
$N^{16}O^{37}Cl$	96·1786	90·2592	5·9194
$N^{18}O^{35}Cl$	99·0621	92·9403	6·1219

Molecular Structure.—A knowledge of the change of molecular moments of inertia produced by isotopic substitution of both chlorine and oxygen makes it possible to determine the structure without recourse to the moments themselves.[4] Both co-ordinates

---

[2] Rogers, Pietenpol, and Williams, *Phys. Rev.*, 1951, **83**, 431.

[3] Knight and Feld, *Phys. Rev.*, 1948, **74**, 354A; Schwendeman, " A Table of Coefficients for the Energy of a Near Symmetric Top." See *J. Chem. Phys.*, 1959, **27**, 986.

[4] Kraitchman, *Amer. J. Phys.*, 1953, **21**, 7; Costain, *J. Chem. Phys.*, 1958, **29**, 864.

of the oxygen atom, referred to principal axes of inertia, can be determined directly from the inertial changes produced by ^{18}O substitution. Only a single co-ordinate of the chlorine atom can be settled in this way, since this atom is so close to the *a*-axis that the change in I_a on substitution is extremely small. The remaining chlorine atoms co-ordinate and both those of the nitrogen atom may be fixed by the first- and second-moment equations $\sum m_i x_i = \sum m_i y_i = \sum m_i x_i y_i = 0$, x_i and y_i being the in-plane co-ordinates referred to principal axes.

The structure obtained in this way is not as sensitive to small changes in the moments as is that obtained by using only information on $N^{16}O^{35}Cl$ and $N^{16}O^{37}Cl$. If errors of $\pm 0{\cdot}10$ Mc./sec. are assigned to the rotational constants B and C, then permutation over all combinations of values for the three isotopic species yields a structure within the range:

$$r_{\mathrm{NCl}} = 1{\cdot}975 \pm 0{\cdot}005\ \text{Å} \quad r_{\mathrm{NO}} = 1{\cdot}139 \pm 0{\cdot}012\ \text{Å} \quad \angle\mathrm{ONCl} = 113^\circ 20' \pm 40'$$

It is difficult to be certain what error should be ascribed to the rotational constants, for, although the comparison of calculated and observed frequencies in Table 1, 2, and 3 indicates a value of about $\pm 0{\cdot}10$ Mc./sec., there may be some undetected effect arising from the presence of unresolved nitrogen hyperfine structure, but from the width of the lines this seems unlikely to be serious. The structure is that which satisfies the changes in B and C on isotopic substitution. Because of a lack of direct information about A, it has not been possible to obtain the inertial defect and use it to gain an idea of the effect of zero-point motion on the parameters obtained.

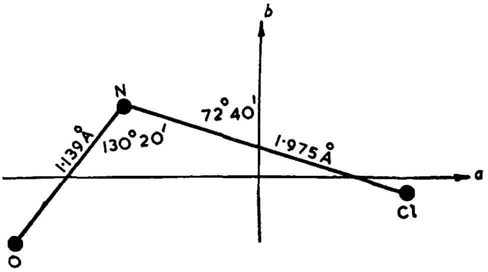


FIG. 1. *Structure and principal axes of the nitrosyl chloride molecule.*

The orientation of the principal axes for the $N^{16}O^{35}Cl$ molecule is shown in Fig. 1. It is these axes to which the nuclear quadrupole coupling coefficients in Table 4 refer. By making the assumption that the N–Cl bond is a principal axis of the coupling tensor, the coupling coefficients along and perpendicular to the bond have been found. Comparison is made in Table 7 with the coefficients for NO_2Cl, the only other molecule containing an N–Cl bond for which such information is available.[5]

TABLE 7. *Comparison of* ^{35}Cl *nuclear quadrupole coupling parameters.* (x *refers to the* N–Cl *bond-direction*; y *and* z *are the in- and out-of-plane perpendiculars respectively. All values are given in* Mc./sec.)

	χ_{xx}	χ_{yy}	χ_{zz}	$\chi_{yy} - \chi_{zz}$
NOCl	−57·2	37·9	19·3	18·6
NO_2Cl	−94·28	51·23	43·05	8·18

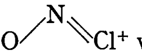
The coupling coefficients for nitryl chloride are derived directly from the experimental data, since in this case the N–Cl bond direction is also a principal axis of inertia, and there can be no doubt about the deviation from axial symmetry reflected in the difference between χ_{yy} and χ_{zz}. The effect has already been interpreted as indicating about 5% double-bond character.[5] The χ-values for nitrosyl chloride do not have quite the same status since, in this case, they have been obtained by a transformation of the coefficients along the principal axes of inertia, on the assumption that the N–Cl direction is a principal

[5] Millen and Sinnott, *J.*, 1958, 350.

axis of the quadrupole coupling tensor. The dependence of the difference $\chi_{yy} - \chi_{zz}$ on the angle θ assumed between the tensor axis and the NCl direction is as follows: *

θ	$-3°$	$-2°$	$-1°$	0	$+1°$	$+2°$	$+3°$
$\chi_{yy} - \chi_{zz}$ (Mc./sec.)......	15·6	16·5	17·5	18·6	19·8	21·1	22·5

Negative values of θ indicate a direction corresponding to a bent bond bowing in towards the oxygen atom. This supposition would reduce somewhat the double-bond character as indicated by $\chi_{yy} - \chi_{zz}$. No assumption regarding θ will reduce the difference below 10 Mc./sec., and this minimum value is attained for the highly unlikely situation where $\theta = 14° 23'$, for which the tensor axes coincide with the inertial axes. It appears that the N–Cl bond has a greater double-bond character for nitrosyl chloride than for nitryl chloride; when θ is taken as zero the double-bond character as measured by electron-loss from the p_z orbital is found to be 10·3%.

An even more striking difference between the two chlorides is that in the field gradients along the bonds. A much greater ionic character for nitrosyl chloride is clearly indicated. If the chlorine orbital used in bond formation is taken as pure $3p$ and the importance of the overlap integral may be neglected in normalisation, then the importance of the ionic contribution NO^+Cl^- is found to be approximately 40%. The two assumptions made here operate in opposite directions, and probably have a better justification in this case than for most bonds. The bond is long (1·975 Å) and so, first, the overlap integral is reduced, and secondly, overlap considerations do not favour appreciable *s*-hybridisation of the chlorine bonding orbital. It is noteworthy that the higher ionic character (NO^+Cl^-) for nitrosyl chloride than for nitryl chloride is accompanied by larger double-bond character  which partially offsets the charge separation.

The high value for the bond length is itself, of course, an indication of the importance of ionic character.[6] Few N–Cl bond lengths are available for comparison. That in Me_2NCl ($r_{N-Cl} = 1·77$ Å) is appreciably shorter,[7] though this may be due partly to different hybridisation about the nitrogen atom. Comparison with nitryl chloride ($r_{N-Cl} = 1·840$ Å) is probably better since the ∠ONCl angles for both molecules are very similar. The increase of 0·14 Å in passing from nitryl to nitrosyl chloride is taken to be an indication of the much greater ionic contribution in the latter case.

The ionic character is also reflected in the N–O bond stretching force constant. A value of 14*md*/Å has been reported [8] for nitrosyl chloride. According to a correlation [9] which has been made for N–O bond stretching force constants, this indicates an N–O bond order of about 2·4.

EXPERIMENTAL

Preparation of $N^{18}OCl$.—*Electrolytic preparation of* ^{18}O*-enriched oxygen.* The route used for the preparation of nitrosyl chloride containing approximately 90% of ^{18}O was to use oxygen prepared by the electrolysis of ^{18}O-enriched water for the oxidation of ammonia and then to cause the resulting oxides of nitrogen to react with hydrogen chloride.

An electrolytic cell (Fig. 2) was designed to electrolyse about 0·6 ml. of water, leaving a residue of less than 0·1 ml. The cell consists of a 3 cm. length of capillary tubing (2 mm. internal diameter) bent to form a U-tube, which is connected to wider-bore tubing (6 mm. internal diameter) which contains nearly the whole of the water to be electrolysed. (The capacity of the U-tube is 0·09 ml.) Electrodes are provided as platinum wires which extend past the capillary tube.

---

* Since the measured coefficients for $N^{18}OCl$ and $N^{16}OCl$ refer to different inertial axes it might be thought that the coefficients for the two molecules determine *θ*. However, the principal axes are rotated only by about 40′ on ^{18}O-substitution and the effect on the *eQq*'s is too small to be of use.

[6] Ketelaar and Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2629.

[7] Stevenson and Schomaker, *J. Amer. Chem. Soc.*, 1940, **62**, 1813.

[8] Burns and Bernstein, *J. Chem. Phys.*, 1950, **18**, 1669; Landau and Fletcher, *J. Mol. Spectroscopy*, 1960, **4**, 276.

[9] Millen, Polydoropoulos, and Watson, *J.*, 1960, 687.

In operating the cell, electrolytic hydrogen and oxygen were collected in flasks connected to the appropriate limbs. It was necessary during the collection of the gases to avoid building up even a small pressure difference across the cell, for this would displace the electrolyte and reduce the fraction which could be electrolysed. For this purpose a differential device illustrated in Fig. 3 was connected to the collecting flasks and to the electrolytic cell at the points marked A. It consists of 200 ml. flasks inserted into each arm and interconnected by a three-way tap. Each flask is half-filled with silicone oil, thus providing a collecting volume of approximately 800 ml. for hydrogen and 400 ml. for oxygen. These volumes were made as closely as possible in the ratio 2 : 1. Because of the large surface area of the silicone oil a small pressure change will correct for any small deviation from the volume ratio 2 : 1. The device has a differential-volume change of approximately 60 ml. per mm. Hg difference in pressure.

Approximately 0·7N-sodium hydroxide was used as electrolyte. This was prepared by using a capillary-tube technique to dissolve oxide-free sodium in the enriched ^{18}O water. It was found in a number of exploratory runs with normal water that more dilute solutions suffered from disadvantages: first, the greater electrolytic heating led to a tendency to bubble formation which often stopped the electrolysis; secondly, concentration polarisation caused the current to decrease after a time. Even with the more concentrated solution it was necessary temporarily to close one of the taps from time to time and thus overcome concentration polarisation by mixing the electrolyte. A current of about 50 mA was found suitable, and although only about 1 watt was dissipated in the cell it was cooled in ice-water, as this was found to reduce the possibility of bubble formation, which led to interruption of the electrolysis. The total quantity of electricity passed was recorded in order to calculate the amount of oxygen obtained.

FIG. 2. *The electrolytic cell.*

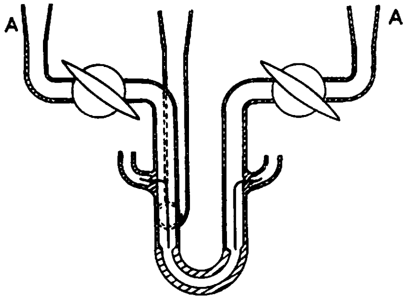
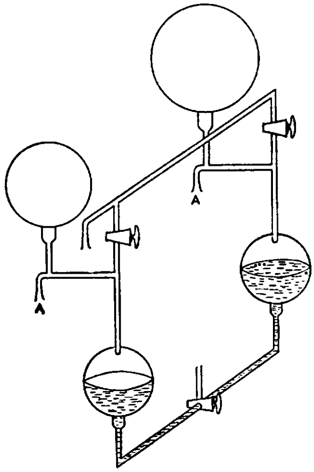


FIG. 3. *Pressure-equalising apparatus.*



Before electrolysis was started, the silicone oil was carefully out-gassed, and the apparatus evacuated. Finally, it was found helpful to introduce about 20 cm. Hg pressure of oxygen-free nitrogen into the apparatus before starting the electrolysis, otherwise undesirable frothing of the electrolyte occurred.

Oxidation of ammonia. Oxygen and ammonia were mixed, passed *via* a flow-meter over heated catalyst, and the products collected. Numerous trial runs were made to find most the favourable conditions. The main problem was to avoid the formation of nitrous oxide and ammonium nitrate or nitrite which represented a loss of oxygen. The main conclusions which are consistent with those reached by Zawadzki [10] from experiments under somewhat different conditions are that the formation of nitric oxide is favoured by (*a*) a high flow rate through the catalyst, (*b*) a high temperature, and (*c*) a short catalyst bed. There were also indications that increasing the proportion of ammonia in the mixture favoured the formation of nitrous oxide.

In the final form of the apparatus a catalyst chamber of fused silica was packed with platinised asbestos for a length of 5 cm. and provided with a heater to operate at about 600° C;

---

[10] Zawadzki, *Discuss. Faraday Soc.*, 1950, **8**, 140.

225 ml. of oxygen at N.T.P. were mixed with 150 ml. of ammonia at N.T.P. and passed over the catalyst, and the product, consisting mainly of dinitrogen tetroxide and a little dinitrogen trioxide, was condensed at −190° c. Excess of hydrogen chloride was admitted and after the reaction was complete the nitrosyl chloride was separated by distillation.

Normal Nitrosyl Chloride.—This was prepared by passing pure nitrogen dioxide through a column of moist potassium chloride.

Observation of Spectra.—Spectra were observed by using a Stark-modulated spectrometer whose main constructional features have been described previously.[5] The absorption cells were cooled in solid carbon dioxide and the sample flowed through continuously. For much of the work 2K33 klystrons were used, and some use was made of R5222 tubes in the various available interchangeable cavities. For the region above 30 kMc./sec. E.M.I. klystrons VX 5023 were employed. The observation of several lines in the region 10—11 kMc./sec. was made possible by the use of the E.M.I. klystron cavity type 25182.

We are indebted to the University of London for the award of a Studentship Grant (to J. P.), to Dr. I. Dostrovsky, of the Weizmann Institute of Science, for arranging the supply of 89% ^{18}O-enriched water, and to E.M.I. for a prototype klystron cavity type 25182. We appreciate the continued interest of Professor Sir Christopher Ingold, F.R.S., and Professor E. D. Hughes, F.R.S.

William Ramsay and Ralph Forster Laboratories,
University College, Gower St., London, W.C.1.
[Present address (J. P.): Physical Chemistry Division,
Imperial Chemical Industries Limited, Plastics Division,
Welwyn Garden City, Herts.]
[*Received, August* 18*th*, 1960.]